GCEP Progress Report for Advanced Transportation

Transportation Vehicle Light-Weighting with Polymeric Glazing and Mouldings

Investigators

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Abstract

Polymeric glazing and mouldings are an extremely high "want" from the transportation community, enabling more creative designs as well as improved part consolidation。 However, plastic windows and mouldings must have high-performance and low-cost protective coating systems with lifetimes in excess of 10 years. Current polymeric glazings do not meet durability/performance requirements for near-term implementation. Our project targets new coating system manufacturing to address durability and cost issues necessary to meet or exceed transportation engineering requirements.

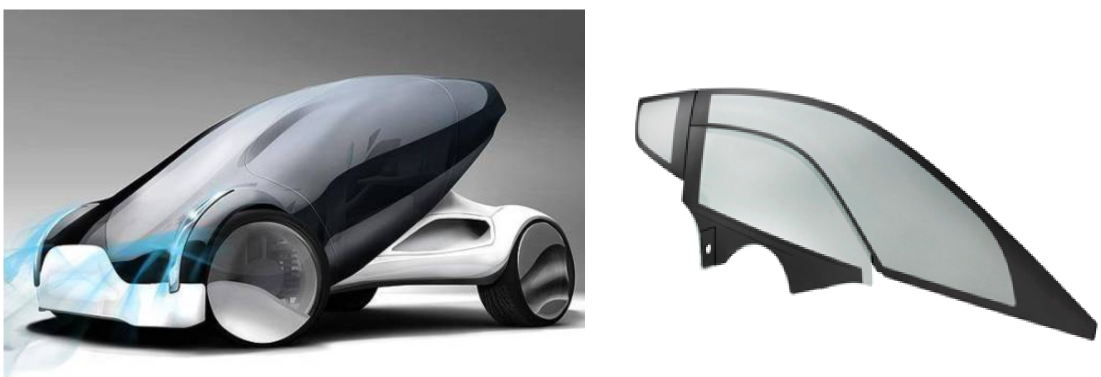
Atmospheric plasma deposition (APD) is an emerging technique that enables plasma deposition of coatings on large and/or complex geometry substrates in ambient air without the need for expensive vacuum or inert manufacturing platforms. It is an environmentally friendly and solvent-free technique, minimizing chemical waste throughout the process as well as greenhouse gas emissions when compared to current wet chemistry aqueous sol-gel manufacturing techniques. Low deposition temperatures (<50°C) allows the deposition on plastic and organic substrates.

Using our state-of-the-art APD coating capabilities, we have demonstrated the ability to deposit highly transparent bilayer organosilicate coatings with superior combinations of elastic modulus and adhesion compared to commercial sol-gel coatings. The bilayer is deposited on large substrates by atmospheric plasma, in ambient air, at room temperature, in a one-step process, using a single inexpensive precursor. The significantly improved elastic modulus translates into improved durability and resistance to scratching and environmental degradation. The method overcomes the challenge of fabricating coatings with both high mechanical and interfacial properties in a one-step process – this would generally require at least a three-step process that includes a surface preparation step, and two coating operations. In APD, the surface is functionalized simultaneously as the first layer is deposited, thereby reducing the total number of processing steps. In this way, we can deposit a tough carbon-bridged hybrid silica layer with excellent adhesion to plastics followed by the deposition of a top layer formed of a dense silica with high elastic modulus, hardness and scratch resistance. The bilayer structure exhibited a remarkable ~100% visible transmittance, twice the adhesion energy and three times the elastic modulus of commercial polysiloxane sol-gel coatings currently in use today for aerospace applications.

Introduction and Background

Polymeric glazing and mouldings are an extremely high "want" for the transportation community. They enable more creative design and improve part consolidation. Polymeric glazing and mouldings are inherently lightweight materials that may find exciting opportunities in the transportation industry as a means of increasing fuel efficiency. With 75% of fuel consumption relating directly to vehicle weight, potential weight reductions that result in an improved price-performance ratio promotes the use of lightweight materials [1]. Generally, polymeric glazing and mouldings can reduce weight by as much as 15 kgs per vehicle for glazing alone. Considering both the mature U.S. market and the emerging Chinese market, there is the potential for staggering reductions in vehicle weights, totalling 195 million kg and 450 million kg for the U.S. and China respectively. Globally, this figure sores above 1 billion kg in possible weight reduction.

One of the key plastics used in automotive sector is polycarbonate (PC). PC has dominated the market for vehicle headlamp covers for 15 years, and now it challenges glass in windows. Plastics are lightweight materials ideal to improve fuel efficiency and design flexibility without compromising on performance or safety. Polymeric moulding processes enable glazings to be formed into shapes that are not feasible with conventional glass forming processes. This technology is therefore seen as one of the key enablers for future design leadership and is currently unavailable due to performance shortcomings. **(Fig. 1)**



(a) (b)

Fig.1: (a) The concept car designed and manufactured by polymeric glazing and mouldings, (b) The side window fabricated by PC on Volkswagen hybrid concept car XL1[1].

Transparent and high-performance coatings on plastic substrates offer the possibility of significant light-weighting and improved aerodynamic design for transportation vehicles. For example, weight reduction together with significant lowering of vehicle center-of-mass can be achieved by replacing automobile glass with plastic (poly-methyl methacrylate (PMMA), polycarbonate (PC) or polyvinyl) windows. Low-cost, light weight and recyclable reinforced organic mouldings can also be used to replace metallic mouldings and improve the aerodynamic design envelope. However, the use of plastic windows and mouldings must have high-performance and low-cost protective coating systems with lifetimes in excess of 10 years. Current polymeric glazings do not meet durability/performance requirements for near-term implementation. For example, current commercial sol-gel based polysiloxane coatings for plastic windows in commercial aerospace systems do not have the desired combination of low-cost processing, weather and scratch resistance, along with long-term durability in terrestrial environments. Our project will target new coating system manufacturing to address durability and cost issues necessary to meet or exceed transportation engineering requirements. An experimental approach based on fundamental chemistry exploits innovative deposition and coating technologies with detailed surface analytical measurements and targeted physical testing.

Atmospheric plasma deposition is an emerging technique that enables plasma deposition of coatings on large and/or complex geometry substrates in ambient air without the need for expensive vacuum or inert manufacturing platforms. It is an environmental friendly technique with the advantage of minimal chemical waste throughout the process and is solvent-free with the potential for zero greenhouse gas emissions compared to current wet chemistry aqueous sol-gel manufacturing techniques. Low deposition temperatures (<50°C) allows the deposition on plastic and organic substrates.

Results

Using our state-of-the-art atmospheric plasma deposition coating capabilities, we have recently demonstrated the ability to deposit highly transparent bilayer organosilicate coatings with superior combinations of Young's elastic modulus and adhesion compared to commercial sol-gel coatings **(Fig. 2)**. The bilayer is deposited on large substrates by atmospheric plasma, in ambient air, at room temperature, in a one-step process, using a single inexpensive precursor. The significantly improved Young's modulus translates into improved durability and resistance to scratching and environmental degradation. The method overcomes the challenge of fabricating coatings with both high mechanical and interfacial properties in a one-step process – this would generally require at least a three-step process that includes a surface preparation step, and two coating operations. Deposition of the bottom coating includes the ability to simultaneously functionalize the surface while depositing a tough carbon-bridged hybrid silica layer with excellent adhesion to plastics followed by the deposition of a top layer formed of a dense silica with high Young's modulus, hardness and scratch resistance. The bilayer structure exhibited a remarkable ~100% visible transmittance, twice the adhesion energy and three times the Young's modulus of commercial polysiloxane sol-gel coatings currently in use today for aerospace applications. [2]

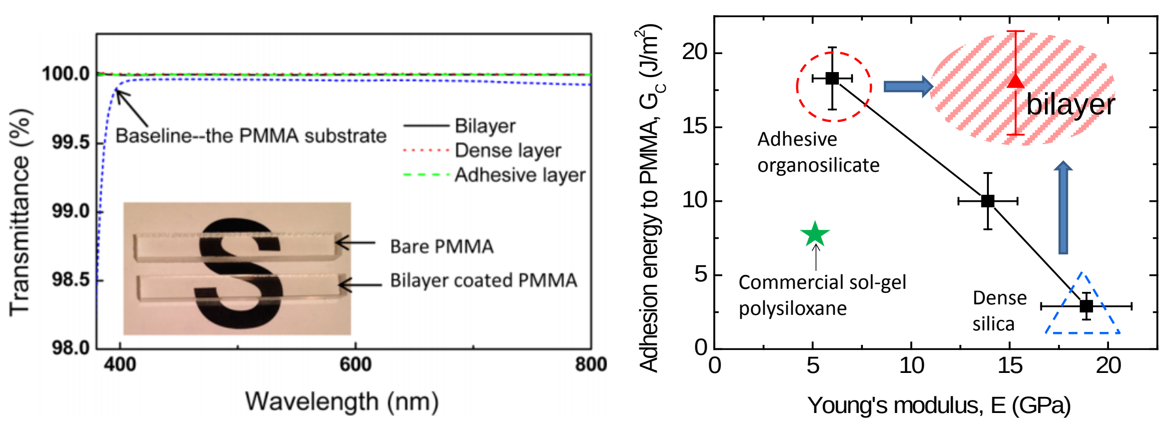


Fig. 2: High-performance and transparent bi-layer coating on PMMA deposited using atmospheric plasma has much better combination of Young's modulus (scratch resistance) and adhesion (durability) compared to commercial sol-gel polysiloxane coatings [2].

We also investigated and summarized the strategy of carbon bridge incorporation into the coating's molecular network. As an open air technique, the abundant oxygen in air during atmospheric plasma deposition poses a significant oxidation challenge for incorporating specific oxygen sensitive components in the coating. Results from our current GCEP program have demonstrated that organic components can be incorporated into molecular structure of hybrid films using atmospheric plasma deposition using several different techniques to produce either high toughness or high stiffness hybrid films. Two key processing parameters were found for successful carbon-bridge incorporation. One was to provide similar or higher concentration of precursor molecules compared to the reactive oxygen species, and the other is to have selected carbon bridges already present in the precursor like in BTESE.

In addition to a single precursor deposition strategy, we also successfully developed the possibility of using dual precursors including an inorganic silane precursor and a purely organic precursor. Compared to other silicate precursors, TEOS is low cost and widely used for silicate coating deposition. It has relatively higher vapor pressure (~1.5 Torr at 23˚C) which enables a lower delivery temperature. The dense silica coatings deposited using TEOS by atmospheric plasma deposition were shown to have the highest Young's modulus compared to other precursors.

However, the deposited silica coatings using TEOS have a low adhesion (~2 J/m^2) with polymer substrates such as PMMA. To solve this challenge, we first demonstrate the deposition of a bottom adhesive layer comprising an adhesive organic-inorganic hybrid layer deposited using dual 1, 5 Cyclooctadiene (CYC) and TEOS precursors. CYC is volatile at room temperature and reactive during plasma deposition due to the two double bonds in the molecular structure, which undergo ring opening and subsequent incorporation into the coating's molecular network. We show that the addition of the CYC precursor significantly increased the carbon content and plasticity of the deposited coating. A dense silica top layer with high hardness and Young's modulus was then deposited using TEOS. The bilayer coating exhibited ~100% transmittance in the visible wavelength region, twice the adhesion energy and a ~5-fold the Young's modulus compared to commercial polysiloxane sol-gel coatings.

We demonstrate the deposition of transparent organosilicate protective bilayer coatings on poly methyl methacrylate (PMMA) substrates with different carbon chain length dipodal silane precursor using atmospheric plasma deposition in ambient air. The bottom adhesive layer was a hybrid organosilicate adhesive layer deposited using either single bis(triethoxysilyl) methane (BTESM), bis(triethoxysilyl) ethane (BTESE), or bis(trimethoxysilyl) hexane (BTMSH) precursor or accompanied with a ring structure 1,5-cyclooctadiene (CYC) precursor. **(Fig. 3)**

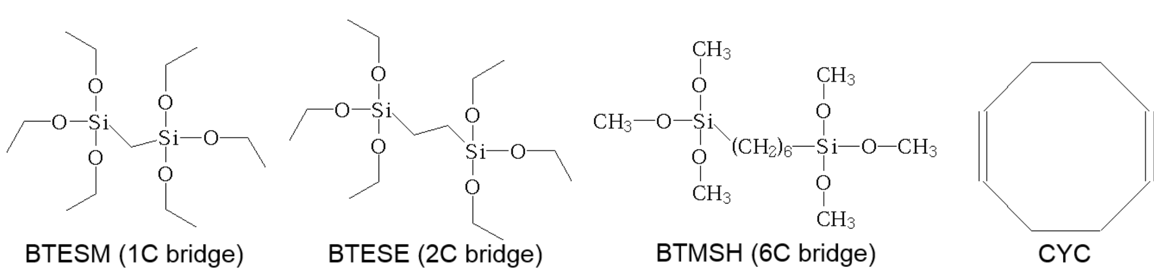


Fig 3. Molecular structures of three carbon bridged precursors and organic CYC precursor. [3]

The deposited coating top layer was a dense silica coating with high elastic modulus and hardness deposited with a single precursor (BTESM, BTESE, and BTMSH). The adhesion energy of bottom adhesive layer showed a distinct enhancement with PMMA substrates compared to commercial polysiloxane sol−gel coatings and increased with increasing carbon bridge length of precursors. The density, hardness, elastic modulus of top hard layer decreased with increasing carbon bridge length of precursors. **(Fig. 4)** The deposited bilayer structure showed ~100% transparency in the visible light wavelength region, ~3 times the adhesion energy and four times the Young's modulus of commercial polysiloxane sol-gel coatings.

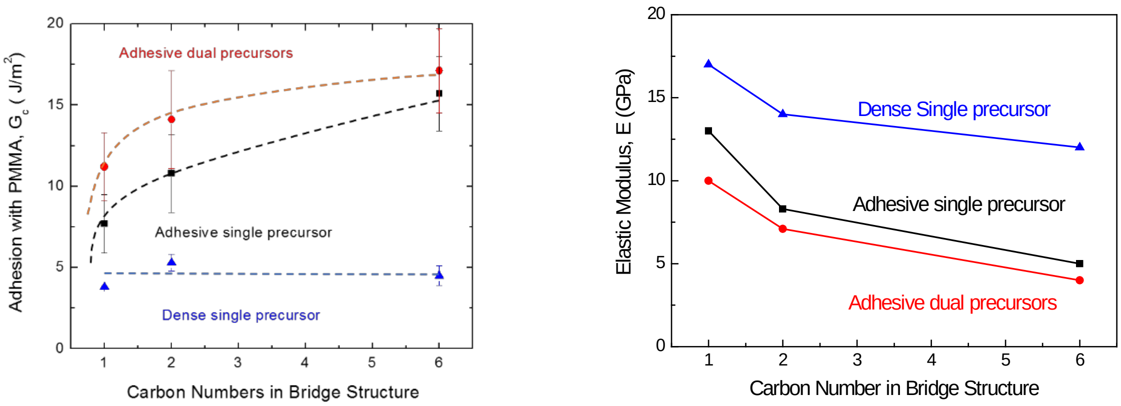


Fig. 4 The relationship between carbon number in the bridge structure to the adhesion with the polymer substrate and modulus of deposited coating.

Progress

We focused on novel bi-layer and hybrid transparent hard coatings on plastic substrates (PMMA, PC, polyvinyl and other polymers). We have innovated with deposition and investigation of various silica coatings, including dense silica coatings and adhesive organosilicate coatings. In addition, we studied carbon bridge incorporation in organosilicate coating deposition systematically. We explored the possibility to use dual precursor strategy to further improve the hardness and adhesion of the coatings.

Future Plans

Demonstrated Protective Coatings: We have demonstrated our ability to deposit highly transparent organosilicate coatings on plastics by a one-step atmospheric plasma deposition process with superior combinations of Young's elastic modulus and adhesion compared to sol-gel coatings. This technique, highly suitable for thermolabile substrates, has been effectively used to coat PC and PMMA with high performance protective coatings.

Incorporate UV Protection: In an attempt to enhance the sustainability of plastics for advanced transportation systems, the next step will be to promote appropriate multifunctional properties to the thin films which will prevent damage of the surface from both scratches and UV radiation, while preserving the high transparency of the material. To address this issue, there will be two strategies adopted. The first strategy seeks to incorporate nanoparticles into a host organosilicate matrix, taking into account our previous works. The incorporation of nanoparticles such as metal oxides (e.g. TiO2, ZrO2, SiO2) into the coating should protect the polymer substrate against mechanical and photo-degradation, while the matrix can still provide enhanced adhesion to the substrate, durability and resistance to scratching and environmental degradation. Nanocomposite deposition will be carried out by atomizing a colloidal solution containing the nanoparticles suitably dispersed with the precursor into a cold plasma operating in air, at atmospheric pressure and room temperature. The second strategy leverages our experience with dual organic and inorganic APD, and aims to incorporate UV-absorbing organic structures into the film. Notably, aromatic compounds absorb in the UV, and through our dual precursor method, we expect that the incorporation of aromatic functionalities will significantly mitigate UV photo-degradation. It is expected that both strategies will realize significant gains for the reliability of the protective coating.

Other Functional Coatings: In addition to increased reliability, we are concerned with improving and exceeding current expectations for optical properties. Currently, our chemistries result in a highly transparent and protective layer. However, as we develop more advanced coatings strategies which involve nanoparticles or hybrid organic/inorganic structures, we expect some degradation in optical performance. In order to impart further functionality to the coated plastics, we expect the addition of an anti-reflective layer to be of great value, particularly for window pane applications. Through our experience in APD, we have developed strategies to modulate the refractive index and absorption in metal oxide systems. Through careful manipulation of plasma parameters and composition, we can tune the atomic composition and therefore the optical properties of metal oxide thin films. By employing a similar strategy, we expect to be able to effectively modulate the refractive index and therefore the films anti-reflective properties of the silica films. We will also separately explore the deposition of a mesoporous silica matrix as an avenue for creating optically graded coatings. By nebulizing a soluble organic molecule into the deposition zone, we expect to form a hybrid silicate-organic structure. Through to-be-determined processing, we will remove the organic phase from the material, resulting in a porous silica structure. By leveraging our expertise in reliability, we will be able to optimize these structures to exhibit excellent optical and mechanical properties.

Process Diagnostics: we are currently bringing a new mass spectrometer detection tool online, which should greatly enhance our insight into atmospheric plasma chemistry. The possibility to use in-situ gas chromatography with mass spectrometry (GC-MS) detection to analyze exhaust gases can provide further insights into the deposition mechanisms as well as provide an efficient manner to carefully monitor the plasma process. This system will allow us to both evaluate precursor reactivity and aid in the identification and quantification of the most abundant stable by-products generated by plasma dissociation. It should then be possible to correlate the plasma chemistry with the chemical composition and structure of the elaborated coatings and to report the main plausible reaction pathways occurring during deposition. Beyond improving the understanding of the underlying fundamental aspects of atmospheric plasma chemistries, this capability should act as an effective tool to improve the properties of our coatings and push forward the performance of our materials.

Publications and Presentations

Publications

1. Siming Dong, Jiahao Han, Zhenlin Zhao, Reinhold Dauskardt, “Role of Carbon Bridge Length of Organosilicate Precursors on the Atmospheric Plasma Deposition of Transparent Bilayer Protective Coatings on Plastics”, **Plasma Processes and Polymers**, In Press. DOI: 10.1002/ppap.201600024.

Presentations

1. Siming Dong, Zhenlin Zhao, Reinhold Dauskardt, “Atmospheric Plasma Deposition of Transparent Organosilicate Multifunctional Coatings on Plastics in Air”, **AVS 62nd meeting**, San Jose, CA, Oct 23, 2015.

2. Siming Dong, Zhenlin Zhao, Yichuan Ding, Linying Cui, Reinhold Dauskardt, “Atmospheric Plasma Deposition and Durability of Transparent Functional Coatings”, **SystemX Conference**, Stanford, November 18, 2015.

3. Michael Hovish, Reinhold Dauskadrt, “Atmospheric Plasma Deposition of Anti-Reflection Layers on Silicon in Open Air” **AVS 62nd International Symposium**, San Jose, CA, October 2015.

4. Reinhold Dauskardt, “Atmospheric Plasma Deposition of Transparent and Conductive Films”, invited presentation at the **43rd International Conference on Metallurgical Coatings and Thin Films**, San Diego, CA.

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2. Linying Cui, Krystelle Lionti, Alpana N. Ranade, Kjersta Larson-Smith, Geraud Dubois, and Reinhold H. Dauskardt, “Highly Transparent Multi-Functional Bilayer Coatings on Polymers Using Low Temperature Atmospheric Plasma Deposition”, **ACS Nano**, 2014. DOI: 10.1021/nn502161p.
3. Siming Dong, Jiahao Han, Zhenlin Zhao, Reinhold Dauskardt, “Role of Carbon Bridge Length of Organosilicate Precursors on the Atmospheric Plasma Deposition of Transparent Bilayer Protective Coatings on Plastics”, **Plasma Processes and Polymers**, In Press. DOI: 10.1002/ppap.201600024.